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Short communication

Influence of PbO on microstructure and properties of a NiZn ferrite

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Abstract

Densification and microstructure development in PbO-doped NiZn ferrite have been studied with special emphasis on the effect of the PbO amount. Pure $Ni_{0.36}Zn_{0.64}Fe_2O_4$ ferrite powder requires a sintering temperature of about 1300 °C to achieve a density of 5 g/cm^3. A small amount of PbO added to the ferrite powder reduces its sintering temperature by about 200 °C, without degrading material properties. A sintered density of 4.9 g/cm^3 was achieved at 1100 °C with 1.2 wt.% PbO addition. Densification has been found to occur by liquid phase sintering. The PbO addition was also found to prevent exaggerated grain growth by hindering grain boundary motion.

Keywords: B. Microstructure; C. Electrical properties; C. Magnetic properties; D. Ferrites; Additives; Densification

1. Introduction

NiZn ferrite system has been widely studied in the recent years [1–4]. The densification of a pure NiZn ferrite to a reasonably high density is difficult because of the relatively high melting point of some component oxides and low bulk diffusivity. As a result, it is very difficult to obtain a sintered body with density exceeding 90% of the theoretical density using solid state sintering. At the same time, typical NiZn ferrites sinter satisfactorily only above 1250 °C, their microstructure and properties being difficult to control because of the volatility of ZnO at such temperatures.

Two methods were used for reducing the sintering temperature: (a) the incorporation of dopants into the ferrite lattice [1,5] and (b) the use of sintering aids able to form a liquid phase (liquid phase sintering) [2,6].

We have recently succeeded in densifying by liquid phase sintering MgCuZn ferrite by PbO addition. Even a small amount of PbO (0.9 wt.%) was found to promote a good densification [7].

The purpose of the present paper was to investigate the effect of the PbO addition on the sintering temperature, particle morphology and electromagnetic properties of $Ni_{0.36}Zn_{0.64}Fe_2O_4$ ferrite prepared by a conventional processing method.

2. Experimental

A ferrite of $Ni_{0.36}Zn_{0.64}Fe_2O_4$ composition was studied. PbO was added during powder preparation, in amounts of 0.3 to 4 wt.% of the host NiZn ferrite.

ZnO, NiO, Fe_2O_3 and PbO powders were mixed together in distilled water for 2 h using an agate ball mill. After drying, the powders were pressed into toroids and tablets using a uniaxial pressure of $5{\cdot}10^7$ N/m^2 without any lubricant. The green compacts were annealed at 800, 900, 1000, 1100 and 1200 °C for 3 h at each temperature and slowly cooled in air to room temperature.

Sintered densities of specimens d were calculated from the weight and dimensions of the disks. The microstructure was observed by Scanning Electron Microscopy (SEM) on fractured surfaces. The phase structure and lattice constant were determined by powder X-ray diffraction (XRD) using CoK_α radiation.

The initial magnetic permeability μ_i was measured on toroidal samples by a bridge method at a frequency of 1

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kHz. The saturation magnetisation σ_s was measured on spheres (3–4 mm diameter) prepared from the toroidal samples, by a vibrating sample magnetometer, in a field of 5 kOe. The electrical resistivity ρ was measured by a Whetstone bridge on the disk-shaped samples, with silver electrodes. The average grain size D was determined from scanning electron micrographs. As a measure of the grain size, the mean linear intercept was taken.

3. Results and discussion

3.1. Mirostructure evolution

The diffraction patterns for three samples of $Ni_{0.36}Zn_{0.64}Fe_2O_4$ ferrite without and with PbO additions are shown in Fig. 1. A single phase spinel structure was observed for all the samples. No undesirable second phases have been detected. Also, the lattice parameter was the same, irrespective of the presence or absence of the dopant. This means that Pb ions do not enter the spinel lattice because of their large radius (1.33 Å) [8].

Scanning electron micrographs of four compositions sintered at 1100 °C are shown in Figs. 2 and 3. The microstructural features clearly show that the morphology is affected by the dopant, i.e. (i) the mode of fracture changes from predominantly transgranular in the undoped sample to predominantly intergranular in the PbO doped ones and (ii) the grain size increases from 2–3 μm for the undoped sample to about 3–5 μm for PbO doped samples. Furthermore, PbO doping tends to change the initial shape of the grains. It is evident from Fig. 3a that the undoped specimen showed a fine structure with faceted crystallites and many residual pores. By incorporating PbO, the average grain size increased, the crystallites tend to a spherical shape and boundaries become clean and thinner (Fig. 3b). A duplex structure is formed consisting of small grain bridges around large crystallites (Fig. 2c and d).

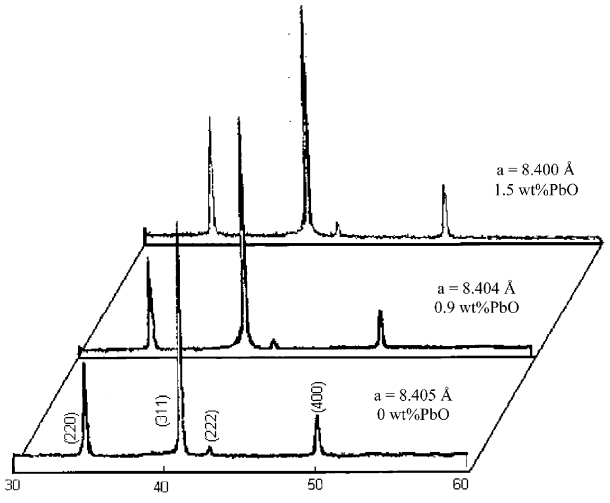

Fig. 1. X-ray diffraction patterns for $Ni_{0.36}Zn_{0.64}Fe_2O_4$ ferrite without and with PbO additive.

The microstructure of the PbO doped ferrites can be explained on the basis of the liquid-phase sintering mechanism [9–13], the formation of grain bridges for 1.5 and 4 wt.% PbO being specific to this sintering mechanism.

3.2. Densification

The influence of PbO addition on the densification of the $Ni_{0.36}Zn_{0.64}Fe_2O_4$ ferrite was investigated. The results in Fig. 4 show that the amount of PbO has a significant impact on the densification behavior of NiZn ferrite. An increase in density was obtained by adding more than 0.6 wt.% PbO and for sintering temperatures higher than 900 °C. At 1100 and 1200 °C, the density reaches its highest values of 4.9 and 5.05 g/cm^3, respectively, for samples doped with 1.2 wt.% PbO. Beyond this doping level, the density slightly decreases because the grain growth causes an intragranular porosity. These results suggest that the concentration of PbO should not be too low to facilitate ferrite sintering, but at the same time, it should not be excessive. The beneficial effect of PbO on the densification of NiZn ferrite can be attributed to liquid phase formation during sintering.

3.3. Effects of PbO content on the magnetic and electrical properties

Fig. 5 shows the variation of electrical resistivity and density vs. PbO content for samples sintered at 1100 °C. Up to 0.6 wt.% PbO, the resistivity slightly decreases. A PbO addition between 0.9 and 1.5 wt.%, i.e. at PbO levels assing best densities and larger grain size, determines a sharp decrease of the resistivity by about one order of magnitude, from $\approx 10^7$ Ω·cm to $\approx 10^6$ Ω·cm. However, the electrical resistivity values of the doped samples remain within reasonable limits for high frequency applications, due to the fine granular structure. When the amount of PbO exceeds 2 wt.%, the electrical resistivity ρ remains practically constant due to the grain boundary resistivity which can be effectively improved by increasing the PbO content.

The influence of the PbO content on the saturation magnetization σ_s and initial permeability μ_i is illustrated in Fig. 6. One can remark that within the optimum doping region of PbO (0.9–1.5 wt.%) the saturation magnetization increases as a result of the dense packing structure of the particles. Higher amounts of PbO lead to a decrease of saturation magnetization σ_s. It is thought that the diffusion rate of Zn ions is much higher than that of any other components in PbO melt and the original cation distribution in NiZn ferrite is disturbed [14].

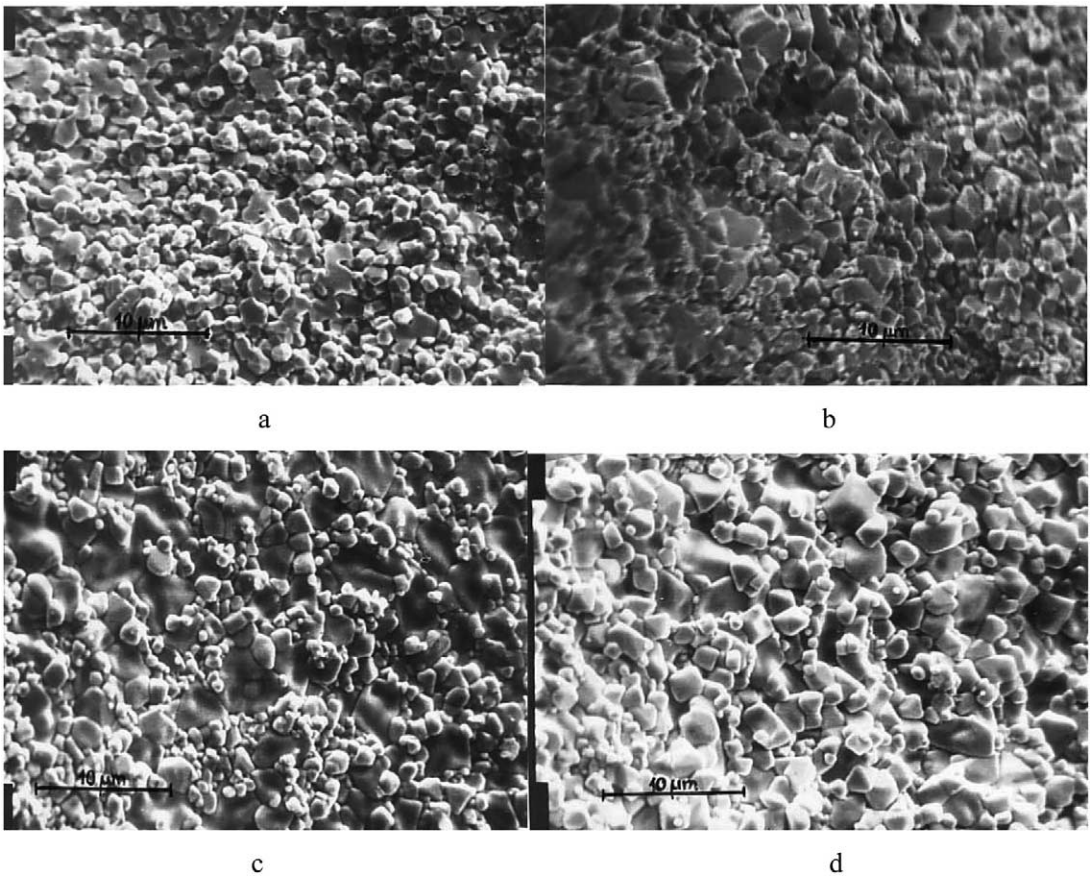

Fig. 2. SEM micrographs of the fractured surfaces of $Ni_{0.36}Zn_{0.64}Fe_2O_4$ ferrite sintered at 1100 °C for 3 h in air: (a) pure NiZn ferrite; (b) NiZn ferrite with 0.9 wt.% PbO; (c) NiZn ferrite with 1.5 wt.% PbO; (d) NiZn ferrite with 4 wt.% PbO. (Enlargement—3000×).

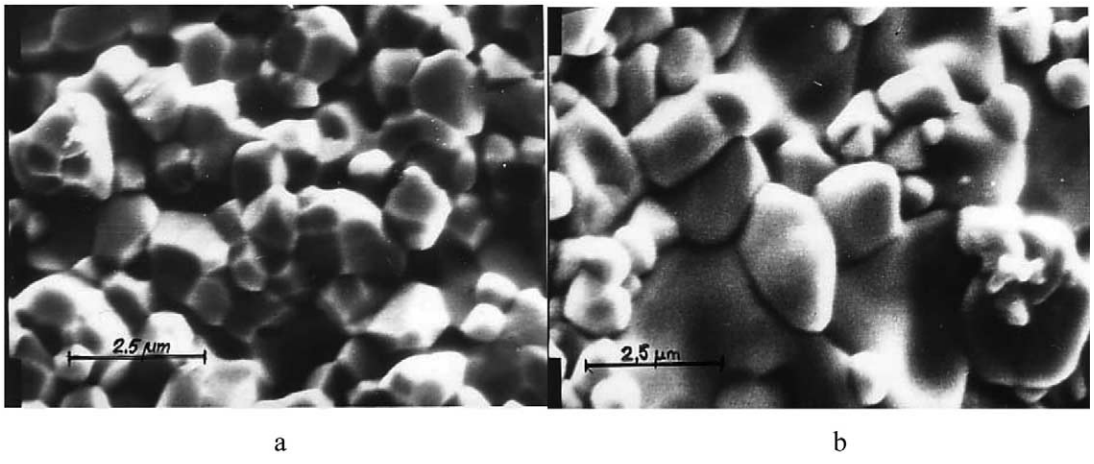

Fig. 3. Enlarged (12 000×) SEM microgrphs for two samples: (a) Pure NiZn ferrite; (b) NiZn ferrite with 1.5 wt.% PbO.

The pure NiZn ferrite sintered at 1100 °C, has an initial permeability μ_i of 394 and this remains practically unmodified for doped samples with 0.9–1.5 wt.% PbO. This result can be correlated with the microstructural evolution shown in Figs. 2 and 3. It is known that the initial permeability of polycrystalline soft ferrites can be described as the superposition of domain wall motion and spin rotation contributions. The small grain size (2–5 μm) suggests that the initial permeability of these ferrites is predominantly rotational in origin, according to the model proposed by Zaag [15].

An interesting result was obtained regarding the temperature dependence of the permeability (Fig. 7). The undoped sample exhibits a continuous decrease of the initial permeability μ_i up to near the Curie point. A good thermal stability of the μ_i for 0.9 wt.% PbO over a

large temperature range (20 to 80 °C) was obtained. For higher additive concentrations, the shape of the μ_i–T curves is greatly modified; the initial permeability μ_i exhibits a maximum near the Curie temperature and then sharply decreases.

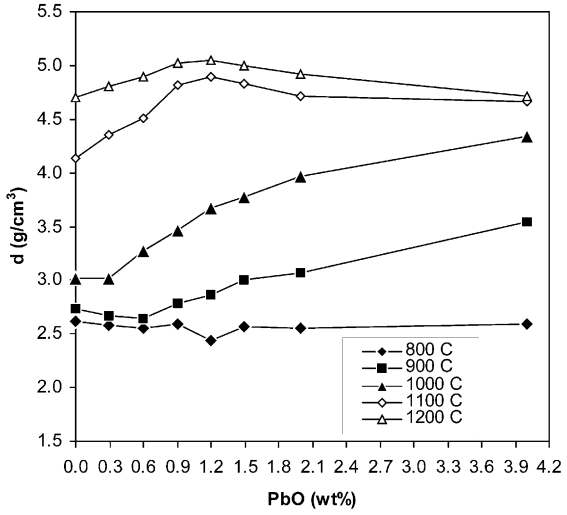

Fig. 4. Sintered density of $Ni_{0.36}Zn_{0.64}Fe_2O_4$ ferrites as a function of PbO additive content, sintered at different temperatures.

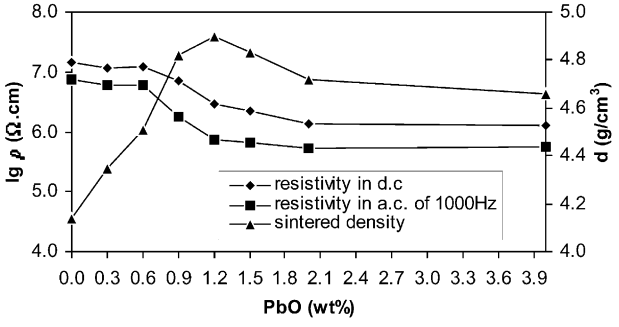

Fig. 5. Electrical resistivities (measured in d.c. and a.c. at 1000 Hz) and sintered density of $Ni_{0.36}Zn_{0.64}Fe_2O_4$ ferrite with the additive content of PbO, sintered at 1100 °C for 3 h in air.

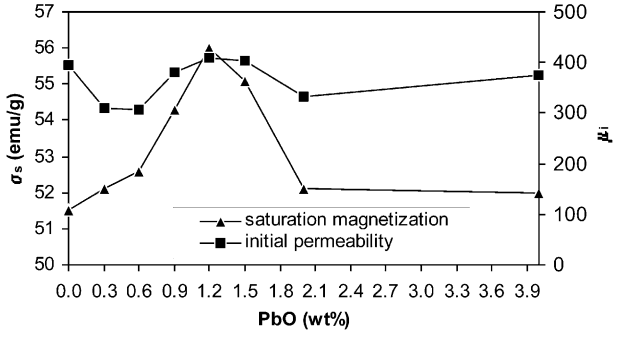

Fig. 6. Influence of PbO content on the saturation magnetization and initial permeability of $Ni_{0.36}Zn_{0.64}Fe_2O_4$ ferrite, sintered at 1100 °C for 3 h in air.

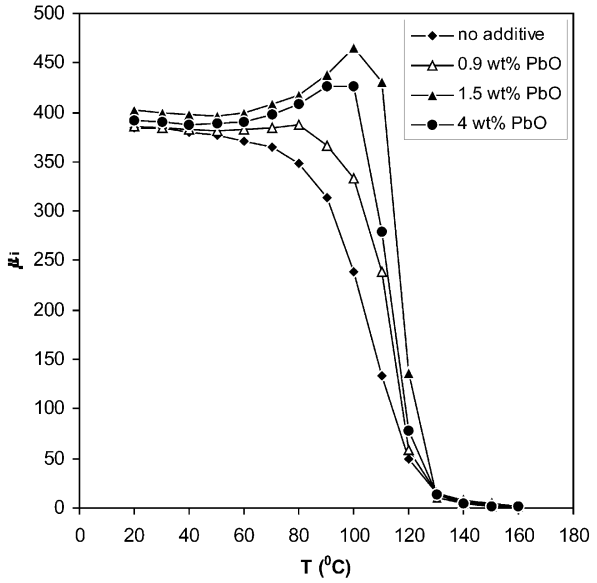

Fig. 7. Temperature dependence of initial permeability for some samples sintered at 1100 °C for 3 h.

4. Conclusions

The sintering behavior and microstructure of NiZn ferrite has been shown to be largely affected by PbO addition. PbO significantly reduces the sintering temperature, thus the energy consumption is minimized and material loss by evaporation is minimized. Low levels of PbO (0.9–1.2 wt.%) are beneficial to the liquid-assisted densification. The resulting micrometer grain size, the increase of the saturation magnetization, the thermal stability of the initial permeability μ_i and the reasonable electrical resistivity suggest that the PbO sintering aid could be commercially attractive for the inexpensive processing of NiZn ferrite at reasonably low temperature (≈1100 °C).

References

[1] J.H. Nam, H.H Jung, J.Y. Shin, J.H. Oh, The effect of Cu substitution on the electrical and magnetic properties of Ni–Zn ferrites, IEEE Trans. Mag. 31 (1995) 3985–3988.
[2] J.Y. Hsu, W.S. Ko, C.J. Chen, The effect of V_2O_5 on the sintering of NiCuZn ferrite, IEEE Trans. Mag. 31 (1995) 3994–3996.
[3] T. Nakamura, Low-temperature sintering of Ni–Zn–Cu ferrite and its permeability spectra, J. Magn. Magn. Mater. 168 (1997) 265–291.
[4] B. Parvatheeswara Rao, P.S.V. Suba Rao, Atmaram Laksham, K.H. Rao, Influence of sintering conditions on the microstructural and electrical properties of NiZn-ferrites, Proc. Int. Symp. on Ferrites in Asia '97, Makuhari, Chiba, Japan, September 1997, J. Magn. Soc. Japan 22 (S1) (1998) 83–85.
[5] E. Rezlescu, N. Rezlescu, C. Pasnicu, M.L. Craus, Densification by nonmagnetic additives of high frequency lithium–zinc and nickel–zinc ferrites, J. Magn. Magn. Mater. 157/158 (1996) 487–488.

[6] K. Hirota, T. Aoyama, S. Enomoto, M. Yoshinaka, O. Yamaguchi, Microstructure and magnetic and electric properties of low-temperature sintering Mn–Zn ferrites without and with addition of lithium borosilicate glass, J. Magn. Magn. Mater. 205 (1999) 283–289.
[7] N. Rezlescu, L. Sachelarie, L. Rezlescu, P.D. Popa, Influence of PbO and Ta_2O_5 on some physical properties of MgCuZn ferrites, Cryst. Res. Technol. 36 (2001) 157–167.
[8] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Cryst. A 32 (1976) 751–769.
[9] H.H. Park, S.J. Cha, D.N. Yoon, Pore-filling process in liquid-phase sintering, Metall. Trans. A 15A (1984) 1075–1080.
[10] T.M. Shaw, Liquid redistribution during liquid-phase sintering, J. Am. Ceram. Soc. 69 (1986) 27–34.
[11] T.H. Courtney, Densification and structural development in liquid-phase sintering, Metall. Trans. A 15A (1984) 1065–1107.
[12] W.D. Kingery, Densification during sintering in the presence of a liquid phase. I. Theory, J. Appl. Phys. 30 (1959) 301–306.
[13] W.D. Kingery, Introduction to Ceramics, Wiley, New York, 1976.
[14] A. Nitta, H. Nakamura, T. Komatsu, K. Matusita, Interface reactions between silicon dioxide-lead oxide glass and manganese zinc ferrite, J. Am. Ceram. Soc. 72 (1989) 1351–1354.
[15] P.J. Van Der Zaag, M. Kolenbrander, M.Th. Rekveldt, The effect of intragranular domain walls in MgMnZn-ferrite, J. Appl. Phys. 83 (1998) 6870–6872.